Separation of the Components of Atmospheric Salt and their Distribution.

By Ken SUGAWARA, Shinya OANA and Tadashirô KOYAMA.

(Received October 2, 1948.)

Introduction. It is a wellknown fact that the splash of sea water is carried up into the air and plays an important role as the primary source of the salt in rain and snow.

Now, it is worth attention that the salt in rain and snow differs so much in composition from sea salt that the ratios Mg: Cl and SO_4: Cl of such salt are larger than those of sea water as shown by H. Lipp[1] of the fog from Mt. Sonnblick and by Y. Miyake[2] of Japanese rain.

As the cause of this difference, we can assume that, by evaporation, there occurs a partial crystallization on the suspending particles of sea water in the air with the production of at least two kinds of daughter particles; the one, hygroscopic in nature and consisting mainly of sodium and chloride, is unstable and falls down earlier from the air, while the other, crystalline in nature and consisting mainly of magnesium and especially of calcium and sulphate, is stable and keeps to remain longer in the air. It is quite natural that these circumstances lead to the relative concentration of the latter kinds of components in the air, which explains well the observations by Lipp and Miyake.

Now, be such a view right, it can be expected that there may occur a distribution of the atmospheric salt with such a variation in composition that the ratios of magnesium, calcium or sulphate to sodium or chloride increase horizontally as we get along from sea coast towards inland, and also we may find a similar distribution vertically as we get higher from sea level upwards.

In the next, be such a variation in salt distribution actually shown, a second question will arise; how does the selective falling down of the unstable components occur?

The present paper deals with these two kinds of problems and answers them by the chemical study of the precipitation, the atmospheric salt itself and also of the salt caught by pine needles on their surfaces from the air.

Horizontal Distribution of the Components of Sea Salt in the Air from Sea Coast towards Inland. Observation was carried out at three stations; the one next sea beach, Sugashima-Island in Ise Bay, the second Nagoya (Higashiyama), 4 km. receding from the head of Ise Bay, and the third the most receding place, Matsumoto, Nagano Pref., 180 km. from

(1) H. Lipp, *Jahresber. des Sonnblickvereins*, **1931**, 27, Wien.
(2) Y. Miyake, *J. Meteorol. Soc. Japan*, **II**, **17** (1939), 20.

CHEMISTRY HALL LIBRARY

the Pacific coast and some 90 km. from Japan Sea.

On more than one hundred samples of rain and snow, taken during 1946–1947, chemical analyses were carried out and their ratios Na: Cl, Mg: Cl, Ca: Cl, and SO_4: Cl determined, the result of which (columns A of Table 1) tells that, as was expected above, the ratios Ca: Cl, SO_4: Cl and also Mg: Cl increase markedly as it recedes into inland.

Table 1.

Ratio in equivalent	Sea water	Rain (A)			Washings of pine needles (B)		
		Sugashima	Nagoya	Matsumoto	Sugashima	Nagoya	Matsumoto
Na/Cl	0.850	0.85	0.90	0.63	0.83	0.85	2.1
Mg/Cl	0.196	0.23	0.31	0.99	0.22	0.27	1.4
Ca/Cl	0.038	0.25	0.31	6.84	0.09	0.55	3.8
SO_4/Cl	0.103	0.35	0.33	2.25	0.17	0.72	2.7

A similar relation is also shown in the salts which were caught by pine needles.

Studies along this line were made as follows: a certain twig was chosen among pine woods and their needles were washed thoroughly with distilled water. After a few days, during which there fell no precipitation, the needles were washed again and the salt, caught by them on their surfaces during the period, was gathered in the washings, of which chemical analyses were carired out.

The Columns B of Table 1 give the result. The increase of Ca: Cl, SO_4: Cl and Mg: Cl is found also here and more evidently.

Vertical Distribution of the Components of Sea Salt in the Air from Sea Level upwards. This kind of distribution is shown by the comparison of the three different kinds of meteorological water-substances; the ordinary rain from 500–1000 m., the fog-ice from the summit of Mt. Fuji (3376 m. high) and the waters of thunderstorm, gathered in Nagoya and in Utsunomiya, Tochigi Pref., the latter kind of water being said to be given rise to at a height of 4–15 km.

The result (Table 2) shows that the ratios Ca: Cl, SO_4: Cl and Mg: Cl grow larger with height, proving a denser distribution of calcium, sulphate and also magnesium relatively to other components in the height.

Table 2.

Ratio in equivalent	Ordinary rain	Fog-ice from the summit of Mt. Fuji	Thunderstorm
Na/Cl	0.90	1.09	2.43
Mg/Cl	0.31	0.40	0.63
Ca/Cl	0.31	1.90	2.19
SO_4/Cl	0.33	1.00	3.24

Ways in which Unstable Components fall down earlier. As to the question, by what processes the unstable components fall down earlier, we can give an answer that there are at least two different kinds of way;

the one the selective washing down by rain and the other selective capturing by various occupants extruding themselves from the earth surface (for examples, shrubs, woods or artificial edifices, etc.) on which some explanations must be given below.

(a) Selective Washing by Rain. This action of rain can be shown from two different sides.

(1) First we can show it by the direct comparison of the composition of atmospheric salt at a certain place to that of the rain which falls there. We can mention one example of Nagoya (Table 3, A, B) in which we find that the values Ca: Na and SO_4: Na are smaller in rain than in the air itself, while the value Mg: Na remains practically constant. The relation is quite comprehensible when we assume that rain prefers sodium, magnesium and chloride to calcium and sulphate in the course of its washing action.

Table 3.

Ratio in equivalent	Atmospheric salt (A)	Salt of rain (B)	Salt caught by pine needles (C)
Ca/Na	1.36	0.34	0.65
Mg/Na	0.30	0.33	0.31
SO_4/Na	0.68	0.38	0.60

(2) The second way which proves the selective washing by rain is indirect and needs a somewhat precise explanation.

First we must make clear the relation between the chloride concentration of rain and the amount of its precipitation. The relation is shown by Fig. 1, drawn from the data of 60 kinds of rain in Nagoya, where

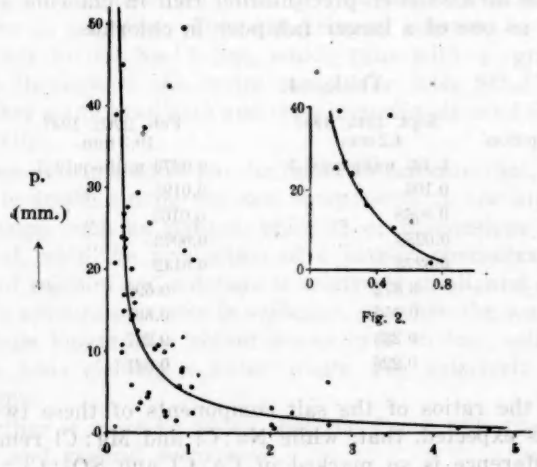


Fig. 2.

Fig. 1.

abscissae denote chloride concentration and ordinates the amount of precipitation.

As it is evident, all the values, except ones with particular nature such as ones of thunderstorm, lie practically on a line of hyperbolic form, expressed by Cl mg./l.$=4.2/p$ mm. The relation is far more evident in the case of rains in rainy season, when practically even meteorological conditions keep to prevail. (Fig. 2)

How can we understand the relation here found?

May we liken it to the case in laboratory where a certain amount of solute is treated with a sufficient or an insufficient amount of solvent?

A dilute solution will be obtained in the former case. The rain of a large precipitation poor in chloride might be likened to this, while another case, where only an insufficient amount of solvent is available, corresponds naturally to a rain of a smaller precipitation rich in chloride.

Now let us go further to imagine a case, where a mixture of a number of solutes, differing in solubility, be treated by solvent. Be the amount of solvent enough in this case, all the mixture will go into solution, while be it insufficient, dissolution will be incomplete and partial, components with larger solubilities going into solution first, and ones less soluble being left unattacked. Can we find the same relation also in the case of rain? Speaking more concretely, can we distinguish two kinds of rain, the one a dilute rain with larger ratios of Ca: Cl and SO_4: Cl, i.e., one the salt composition of which is nearer to that of atmospheric salt, and the other a rather concentrated one with smaller values of Ca: Cl and SO_4 :Cl, which seems to have dissolved the salt in the air partially?

This is actually the case. In order to show it, we had better to begin with examples (Table 4). We may choose the rain of Sept. 13th, 1946 as an example of a smaller precipitation rich in chloride and that of Feb. 20th, 1947 as one of a larger fall poor in chloride.

Table 4.

Amount of precipition	Sept. 13th, 1946 4.2 mm.	Feb. 20th, 1947 10.3 mm.
Cl	0.121 milliequiv./l.	0.0273 milliequiv./l.
Na	0.105 ,,	0.0195 ,,
Ca	0.0068 ,,	0.0163 ,,
Mg	0.0283 ,,	0.0073 ,,
SO_4	0.0273 ,,	0.0142 ,,
Na/Cl	0.872	0.696
Ca/Cl	0.056	0.597
Mg/Cl	0.233	0.267
SO_4/Cl	0.226	0.521

In comparing the ratios of the salt components of these two kinds of rain, we find, as expected, that, while Na: Cl and Mg: Cl remain not differing much, difference is so marked of Ca: Cl and SO_4: Cl that the values of the dilute Sept. 13 rain attain 2–10 times as high as those of the concentrated Feb. 20th one.

Now the relation is no accidental one, particular to the examples cited, but a more general one. This can be shown by Fig. 3 in which, referring to the chloride values (abscissae), the corresponding ones of sodium, magnesium, calcium and sulphate (all expressed in milliequivalent/l.) are taken as ordinates and four kinds of lines, Na-Cl, Mg-Cl, SO_4-Cl and Ca-Cl are drawn.

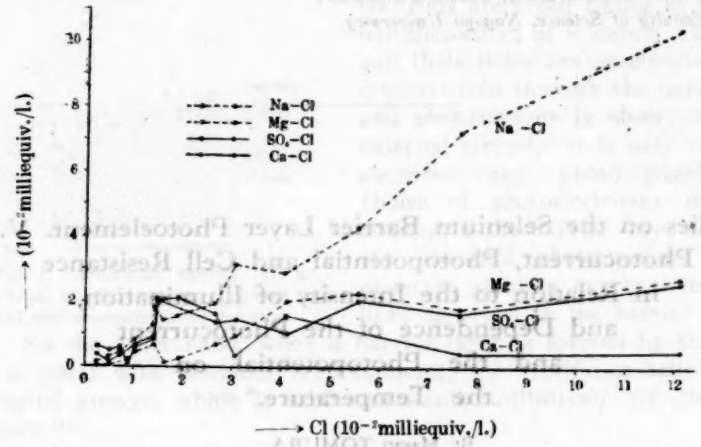


Fig. 3.

The perusal of the lines tells us much of the different behaviours of the individual components in their course of dissolution into rain, but here we must confine ourselves to focus our attention solely upon the point now in question. Then the primary point to be considered is that in contrary to the Na-Cl line, which runs with a gradient practically constant throughout the entire range, the lines SO_4-Cl and Ca-Cl start with rather acute gradients and then immediately tend to run along rather horizontally.

These circumstances can be taken to indicate that, when the amount of rain is small, among the salt components in the air, it chooses more soluble ones, such as sodium, chloride or magnesium and washes down them first, with the production of a rather concentrated water whose content of calcium and sulphate is relatively small, and on the other hand, when the amount of water is sufficient, or when the washing action keeps to continue longer, the action comes over to less soluble calcium and sulphate, thus yielding a water dilute but relatively rich in the latter components.

Further it must be added that the figure tells that such is the case of wide and general occurrence.

(b) Selective Capturing by various Occupants extruding themselves on the Earth Surface. This is shown by the comparison of the

cause of complicated behaviour of the photocurrent, photopotential and cell resistance under different conditions.

Theoretical Calculations. Since the primary photocurrent i is proportional to the intensity of illumination I,

$$i = aI \quad \cdots\cdots (1)$$

is obtained. Here a is a constant. From the above section, furthermore, the next relation exists.

$$i = i_i + i_e \quad \cdots\cdots (2)$$

Since the selenium photoelement has a barrier of pure contact, we may apply Mott's theory to the barrier of pure contact which has a parabolical internal potential. Then we obtain[5]

$$\left.\begin{aligned} i_i &= \frac{2\sqrt{V_0}\sqrt{V_0-V}}{\rho_\infty}\left(e^{\frac{eV}{kT}}-1\right) \\ \rho_\infty &= \frac{d}{evn_0} \\ n_0 &= 2\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} e^{-\frac{eV_0}{kT}} \end{aligned}\right\} \quad \cdots\cdots (3)$$

where V_0 is the contact potential difference between the metal and the semiconductor, V the voltage impressed on R_i, e the charge of an electron, k the Boltzmann constant, T the absolute temperature, d the thickness of the barrier layer, v the mobility of a positive hole, m the mass of an electron and h the Planck constant.

For the case of a cuprous oxide backwall cell having a constant internal field in its barrier layer which was treated by Mott, the next formula is to be taken instead of the equation (3).

$$i_i = \frac{V_0-V}{\rho_\infty}\left(e^{\frac{eV}{kT}}-1\right) \quad \cdots\cdots (3')$$

The equations (3) and (3′) hold only in the range of $V<V_0$ and V cannot exceed V_0 even if I becomes large. It is the easy flow of the rectifying current that goes into our problem, so the image force effect can be neglected.

From the equations (1), (2) and (3), we obtain

$$\left.\begin{aligned} aI &= i_e + \frac{2v\sqrt{V_0}\sqrt{V_0-V}}{\rho_\infty}\left(e^{\frac{eV}{kT}}-1\right) \\ V &= i_e R = i_e(R_f+R_s+R_e) \end{aligned}\right\} \quad \cdots\cdots (4)$$

(5) R. Kubo, private communication.

The equation (4) represents the general relations between the photocurrent, photopotential and cell resistance, and their dependence to the intensity of illumination as well as to the temperature.

(a) Photopotential. Photopotential V_p is defined usually as the open potential of the cell, so V_p is given by making $i_c=o$ in (4). Namely,

$$aI = \frac{2\sqrt{V_0}\sqrt{V_0-V_p}}{\rho_\infty}\left(e^{\frac{eV_p}{kT}}-1\right) \quad \cdots\cdots\cdots\cdots (5)$$

When $eV_p \ll kT$, or I is small and T is large, we have

$$aI = \frac{2V_0}{\rho_\infty}\frac{eV_p}{kT} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (6)$$

from (5), because the condition $V \ll V_0$ holds. Then V_p is proportional to I.

In the range of $eV_p \gg kT$, (5) becomes

$$aI = \frac{2\sqrt{V_0}\sqrt{V_0-V_p}}{\rho_\infty}e^{\frac{eV_p}{kT}} \quad \cdots\cdots\cdots\cdots (7)$$

so V_p is proportional to log I.

(b) Photocurrent. If we put $V=i_cR=i_c(R_f+R_s+R_c)$ into (4), the relations between i_c and I or R are obtained. Especially for the case of $eV \ll kT$,

$$aI = i_c\left(1+\frac{2eV_0R}{\rho_\infty kT}\right)+\cdots\cdots$$

namely,

$$i_c = \frac{aI}{1+\frac{2eV_0}{kT}\frac{R}{\rho_\infty}} \quad \cdots\cdots\cdots\cdots\cdots\cdots (8)$$

is obtained.

Usually i_c for $R_c=0$ is called the short circuit photocurrent, but since R_f and R_s is finite, we cannot obtain the theoretical short circuit current even though we make use of the Campbell Freeth circuit. R_f and R_s are so small compared to the usual external resistance that the practical short circuit photocurrent i_{cs} is obtained as

$$i_{cs} = aI \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (9)$$

by introducing $V=0$ into (4). This equation is right so long as the condition $V=i_c(R_f+R_s) \backsimeq 0$ holds.

(c) Cell Resistance. So called cell resistance is defined as the ratio

of photopotential to the short circuit current at a given intensity of illumination. From (5) and (9),

$$i_{es} = \frac{2\nu\sqrt{V_0}\sqrt{V_0 - V_p}}{\rho_\infty}\left(e^{\frac{eV_p}{kT}} - 1\right) \quad \cdots\cdots\cdots\cdots \quad (10)$$

is obtained. So R_i is given by the next equation.

$$\frac{1}{R_i} = \frac{i_{es}}{V_p} = \frac{2\nu\sqrt{V_0}\sqrt{V_0 - V_p}}{\rho_\infty V_p}\left(e^{\frac{eV_p}{kT}} - 1\right) \quad \cdots\cdots \quad (11)$$

The above defined cell resistance is the ratio of two quantities of two different physical states, so it has no real physical meaning. But as (11) shows, it is a formal easy flow resistance of the barrier layer onto which the photopotential V_p is impressed.

(d) Dependence of the Photopotential on the Temperature. If we consider a case of $eV_p \ll kT$, we can derive the next equation from (6).

$$V_p = \frac{aI}{\beta}\frac{e^{\frac{eV_0}{kT}}}{T^{\frac{1}{2}}} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (12)$$

where $$\beta = 4\left(\frac{2\pi mk}{h^2}\right)^{\frac{3}{2}}\frac{e^2 v V_0}{kd}$$

Namely, V_p decreases exponentially with T.

And then, in the region where $e^{\frac{eV_p}{kT}} \gg 1$ and $V_p / V_0 \ll 1$ hold, we can derive

$$V_p = V_0 + \frac{kT}{e}\log\frac{aIe}{\beta k T^{\frac{3}{2}}} \quad \cdots\cdots\cdots\cdots\cdots \quad (13)$$

from (5) approximately. This equation means that V_p decreases when T increases, because $\log(aIe/\beta kT^{\frac{3}{2}})$ must be negative from (5), that is to say, T must be larger than a definite value.

(e) Dependence of the Photocurrent on the Temperature. In the same manner as (*d*), we can derive the relations between i_e and T, by introducing $V = i_e R$ into (4) and (8). The result is that i_e decreases when T increases.

At low temperatures we must consider variations of a and v with temperature, and the tunnel effect of positive holes through the barrier layer, making increase of i_e. Thus we cannot gain characteristics of photopotential and photocurrent at low temperatures from (3).

Discussions of the Results. In general the results of the preceding sections can be confirmed by experiments.[6] The equation (3) which we

(6) B. Lange, "Die Photoelemente und ihre Anwendnng", Leipzig (1936).

take as the basis of our calculation is purely theoretical, yet it explains quantitatively the characteristics of the selenium cell, although it fails to explain rigorously the minor details of the experimental results. This fact is attributed to the non-uniform nature of the barrier layer which is found also in the case of the selenium rectifier.

As for the cuprous oxide frontwall cell, since its barrier layer is considered as a pure contact of a metal and a cuprous oxide semiconductor and has a parabolical internal field, the results of the above calculations can be applied just in the same way. But the cuprous oxide backwall cell has a barrier layer of a constant internal field,[4] so we must take up the equation (3′) instead of (3). In this case the results are not very different from the above results.

At very low temperature, as above mentioned, corrections must be added. On the other hand, at higher temperatures than room temperatures, selenide formation takes place in the barrier layer as the author has pointed out,[7] so care must be taken in the experiments at the higher temperatures.

Conclusion. By clearing up the relations between the barrier layer photoeffect and rectification of a barrier layer and by applying the Mott's theory of a barrier layer rectifier, the general formula of the relations between the physical quantities of the barrier layer photoelement are derived and their features explained.

Matsuda Research Laboratory of
The Tokyo Shibaura Electric Co., Ltd.

On the Chemical Compositions of the Eruptives of Volcanoes in New Britain, Pacific Ocean.

By Yasuo MIYAKE and Yoshio SUGIURA.

(Received November 12, 1948.)

We have carried out the chemical analysis of lava, lapilli and volcanic sand ejected from the volcano group near the city of Rabaul in New Britain (Bismarck Archipelago).

These volcanoes are Mt. Tavurvur, Mt. Kombiu and Mt. Baluan. Samples for the chemical analysis were collected by Mr. Kizawa, a seismologist of the Central Meteorological Observatory of Japan, in 1942.

(7) M. Tomura, *Proc. Toshiba Lab.*, **19** (1944), 206.

Fig. 1. The volcano group near the city of Rabaul

The present conditions of these volcanoes are as follows. Mt. Tavurvur exploded in 1937, and its volcanic activity has continued until the present day. Mt. Baluan erupted after the explosion of Mt. Tavurvur in 1937, but it is in dormant state now. Mt. Kombiu has two craters. The old one is called Rabalankaia which has been dormant since 1870, and the other is Palagiagia which was active till recent days.

The chemical compositions of the following seven samples have been studied.

Table 1.

No.	Name of Mountain.	Kind.	Colour, etc.	Place of Collection.
1.	Mt. Tavurvur.	Lapilli.	Blackish violet, pumiceous.	East side.
2.	do.	Sand	Pale reddish brown.	do.
3.	do.	Lapilli.	Like No. 1.	Top
4.	Mt. Baluan.	Lapilli.	Black.	do.
5.	Mt. Kombiu. (Rabalankaia)	Lapilli.	Black.	Wall of the crater.
6.	do.	Lava sand.	Blackish blue.	Bottom of the crater.
7.	do. (Palagiagia)	Lava.	Black.	Unknown.

In Table 2 and Table 3, the results of chemical analysis are given.

Table 2.

Chemical Compositions of the Eruptives from Mt. Tavurvur.

	No. 1.	No. 2.	No. 3.	Mean.
SiO_2	48.47 %	46.65 %	48.34 %	47.82 %
TiO_2	0.77	1.17	0.85	0.93
Al_2O_3	18.81	20.11	17.75	18.89
Fe_2O_3	3.70	4.49	4.64	4.28
FeO	6.39	5.96	6.73	6.36
MnO	0.19	0.28	0.23	0.23
MgO	5.68	5.33	5.35	5.45
CaO	12.75	11.40	11.96	12.04
Na_2O	1.94	2.19	3.19	2.44
K_2O	0.53	0.64	0.49	0.55
P_2O_5	0.25	0.31	0.75	0.44
H_2O^+	—	0.01	—	—
H_2O^-	0.23	0.50	0.17	0.30
Total.	99.71	99.04	100.45	99.73

Table 3.

Chemical Compositions of the Eruptives from Mt. Baluan and Mt. Kombiu.

No. 4. Mt. Baluan
No. 5. & No. 6. Mt. Kombiu (Rabalankaia)
No. 7. Mt. Kombiu (Palagiagia)

	No. 4	No. 5.	No. 6.	No. 7	Mean.
SiO_2	61.75 %	59.75 %	60.80 %	59.40 %	60.42 %
TiO_2	1.08	0.87	0.95	0.90	0.95
Al_2O_3	14.44	14.00	15.50	14.81	14.69
Fe_2O_3	3.05	2.06	2.51	3.30	2.73
FeO	3.67	5.01	3.57	3.93	4.05
MnO	0.12	0.09	0.14	0.15	0.13
MgO	1.52	2.61	1.62	2.12	1.97
CaO	7.53	9.16	8.01	9.61	8.58
Na_2O	3.55	3.98	3.48	3.27	3.57
K_2O	1.88	1.91	1.82	2.33	1.99
P_2O_5	0.73	0.54	1.00	0.95	0.81
H_2O^+	0.05	0.21	0.29	0.11	0.17
H_2O^-	0.08	0.07	0.27	0.02	0.11
Total	99.45	100.26	99.93	100.90	100.17

From these results we can find a good similarity among the composition of three samples collected on Mt. Tavurvur. In the other hand, eruptives from Mt. Baluan and Mt. Kombiu have almost the same composition which distinctly differs from those of the eruptives from Mt. Tavurvur. Eruptives from Mt. Tavurvur have low silicic acid content (smaller than 50%) and contain more aluminium, iron, manganese, calcium and magnesium, and less alkalis than those from the other two volcanoes, therefore, they may be called basaltic. On the contrary, eruptives from Mt. Baluan and Mt. Kombiu have comparatively high silicic acid content (almost 60%), and they are quartz-andesitic.

There are old data of chemical analysis of lava and pumice in New Britain by A. Liversidge[1] (1883), which are fairly different from our results. But, as H. S. Washington pointed out, the content of magnesium is too small and manganese is too high in his data and these are not probable. It is of interest to compare the chemical compositions of the erupitves of volcanoes in New Britain with the eruptives of famous volcanoes in Japan. Mean values of those of Mt. Tavurvur and Mt. Kombiu and other data of eruptives in Japan are given in Table 4.

(1) H. S. Washington, "Chemical Analysis of Igneous Rocks," p. 250, 429 Washington, D. C. (1903).

Table 4.

	Tavurvur	Kombiu	Aso[2]	Fuji[3]	Fuji[4]
SiO_2	47.82 %	69.42 %	53.92 %	49.31 %	57.87 %
TiO_2	0.93	0.95	0.85	0.60	0.82
Al_2O_3	18.89	14.69	18.67	19.86	17.80
Fe_2O_3	4.28	2.73	2.69	3.93	3.07
FeO	6.86	4.05	5.93	6.43	5.31
MnO	0.23	0.13	0.14	0.22	0.20
MgO	5.45	1.97	3.80	5.11	2.63
CaO	12.04	8.58	9.27	11.03	6.80
Na_2O	2.44	3.57	2.90	1.97	3.52
K_2O	0.55	1.99	1.86	0.60	1.43
P_2O_5	0.44	0.81	0.27	0.16	0.27
H_2O^+	—	0.17	0.21	0.51	0.91
H_2O^-	0.39	0.11	—	—	—
Total	99.73	100.17	100.51	99.73	100.63

In this Table we can see the resemblance between the chemical compositions of the eruptives of the volcano group near th city of Rabaul and those of Mt. Fuji.

Meteorological Institute, Tokyo, Japan.

The Addition of Hydrogen Bromide to Cinnamic Acid and the Oxygen Effect.[1]

By Osamu SIMAMURA and Makoto TAKAHASI.

(Received November 16, 1948.)

The problem of the oxygen effect in the addition of hydrogen bromide to ethylenic compounds, manifesting itself in the reversal of the direction of addition expected from Markownikoff's rule, appears to have been settled so far as its general character is concerned.[2] The active agents which cause the abnormal addition have turned cut to be bromine atoms produced from hydrogen bromide under relevant experimental conditions.

(2) Y. Miyake and K. Mayama, *J. Met. Soc. Jap.* Ser. II. **16** (1938), 95.

(3) I. Iwasaki, *J. Chem. Soc. Jap.*, **58** (1937), 487.

(4) I. Iwasaki and M. Ikawa, *ibid.*, **59** (1938), 1175.

(1) Presented at the 68th Annual Meeting of the Chemical Society of Japan in Tokyo, October 18, 1946.

(2) For reviews of the subject see Y. Urushibara, *Kwagakusoho*, **6** (1944), 185; F. R. Mayo and C. Walling, *Chem. Rev.*, **27** (1940), 351.

A bromine atom adds to the ethylenic bond to produce a free radical containing bromine, and this reacts with hydrogen bromide yielding a molecule of the final addition product and another bromine atom, the latter in turn attaching itself to another molecule of the ethylenic compound to reproduce the free radical:

$$RCH = CHR' + \dot{B}r \rightarrow RCHBr\dot{C}HR',$$
$$RCHBr\dot{C}HR' + HBr \rightarrow RCHBrCH_2R' + \dot{B}r.$$

Thus a chain reaction occurs, and in each cycle one molecule of the abnormal addition product is produced. However, concerning essential factors deciding the position of attack by the bromine atom and hence the orientation of hydrogen bromide a consensus of opinion has not yet been attained. Furthermore, in such cases as crotonic[3,4,5] and cinnamic[4] acids no reversal has ever been observed, the products under the oxygenic or peroxidic condition being identical with those under the normal condition, and with regard to the mechanism of the phenomena several theories have been set forth by various workers.

The investigation on the addition of hydrogen bromide to crotonic acid reported from this Laboratory[5] was a contribution to elucidation of these moot questions. A small amount of oxygen was found not to influence the addition of hydrogen bromide to crotonic acid either in the direction of addition, β-bromobutyric acid being the sole product, or in the rate of the reaction. The mixture of hydrogen bromide and oxygen, however, reacted with crotonic acid in carbon tetrachloride giving rise to three products, β-bromobutyric acid, crotonic acid dibromide, and α-hydroxy-β-bromobutyric acid. It was therefore concluded that, in the addition of hydrogen bromide to crotonic acid in the presence of oxygen, the oxygen participates in the reaction, as is the case with ordinary ethylenic compounds, producing bromine atoms from hydrogen bromide, and then the bromine atoms attach themselves to the β-carbon atom of crotonic acid to yield a free radical, $CH_3CHBr\dot{C}HCOOH$. The bromo radical gives rise to α-hydroxy-β-bromobutyric acid by a ready reaction, in contrast to radicals from the common ethylenic compounds, with oxygen rather than with hydrogen bromide. If the free radical had abstracted a hydrogen atom from a molecule of hydrogen bromide to yield β-bromobutyric acid and a bromine atom, the usual chain reaction of the abnormal addition would have taken place, and the addition to crotonic acid would have proceeded more rapidly in the presence of oxygen than in its absence. The experimental identification of the β-carbon atom of crotonic acid as the site of attack by bromine atoms supports the theory suggested by Mayo and Walling[2] that of the alternative free radicals which can be produced by addition of a bromine atom the more stable is the one to be preferentially

(3) D. C. Grimshaw, J. B. Guy and J. C. Smith, *J. Chem. Soc.*, **1940**, 68; C. Walling, M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **61** (1939), 2693.
(4) A. Michael and G. H. Shadinger, *J. Org. Chem.*, **4** (1939), 128.
(5) O. Simamura, this Bulletin, **17** (1942), 326.

produced. For the free radical $CH_3CHBr\dot{C}HCOOH$ is considered more stable than the isomeric radical $CH_3\dot{C}HCHBrCOOH$ by the resonance energy due to the conjugation of the odd electron at the α-carbon atom with the carboxyl group, whereas such an effect is absent in the later radical.

Experiments have now been extended to cinnamic acid. According to A. Michael[4] cinnamic acid added hydrogen bromide to give only β-bromohydrocinnamic acid, but the result does not appear to be conclusive, as it does not seem that, in his investigation, due attention was paid to the various factors now accepted as influencing the course of the addition reaction.

Cinnamic acid was subjected to the action of hydrogen bromide in the presence of either benzoyl peroxide or catechol in benzene in a sealed tube kept at 60°C. The product in either case was found to be β-bromohydrocinnamic acid, and no appreciable difference in the reaction velocity was observed. On the other hand, when a mixture of hydrogen bromide and oxygen was passed into a suspension of cinnamic acid (10 g.) in benzene (70–80 c.c.) in the dark for 4 to 7 hours, the reaction vessel being cooled with ice water, a rather vigorous reaction took place with the evolution of heat. In the course of the reaction, water and a deposit, identified as α,β-dibromohydrocinnamic acid (m.p. 192°) as described in the experimental part, separated from the reaction mixture. On evaporation of the filtered benzene solution under reduced pressure at room temperature a residue was obtained, from which α,β-dibromohydrocinnamic acid and ω-bromoacetophenone were isolated. The ω-bromoacetophenone was certainly a scission product formed in the course of the reaction, and the other fragment, carbon dioxide, was found in the gas mixture escaping from the reaction vessel.

From these observations it is quite obvious that hydrogen bromide, oxygen, and cinnamic acid undergo a complicated reaction of just the same type as was already reported from this Laboratory.[6] Thus the course of the reaction is considered to be as follows: The simultaneous action of hydrogen bromide and oxygen on cinnamic acid produces a free radical $C_6H_5\dot{C}HCHBrCOOH$ and an unidentified substance (or substances) of peroxidic nature. α,β-Dibromohydrocinnamic acid is produced by the action of bromine liberated from hydrogen bromide by the action of the peroxidic substance on the free radical $C_6H_5\dot{C}HCHBrCOOH$,[7] a bromine atom being set free to add to cinnamic acid regenerating the same free

(6) Y. Urushibara and O. Simamura, this Bulletin, **14** (1939), 323; O. Simamura, *ibid.*, **15** (1940), 292 and reference 5.

(7) In an investigation of the addition of bromine to cinnamic acid in carbon tetrachloride, one of the present authors (O. Simamura, this Bulletin, **17** (1942), 280) has postulated that the addition takes place through a chain mechanism involving bromine atoms and the free radical which is formed by attachment of a bromine atom to the double bond of cinnamic acid. The structure of the radical was tentatively assumed to be $C_6H_5CHBr\dot{C}HCOOH$ on the basis of evidences available at that time. From the present results it is now concluded that, in that case also, the radical must have the structure $C_6H_5\dot{C}HCHBrCOOH$.

radical. The acid may also be formed by the combined action of hydrogen bromide and oxygen on the free radical. The free radical is so stable that it cannot abstract a hydrogen atom from a molecule of hydrogen bromide to form α-bromohydrocinnamic acid and a bromine atom, which is subsequently to add to cinnamic acid forming the free radical and thus initiating the cyclic process of the chain addition reaction, but the free radical reacts at the β-carbon atom with oxygen, which has more or less unsaturated nature and is present comparatively in abundance in the reacting milieu, and ω-bromoacetophenone eventually is formed after decarboxylation.

There was no evidence to show the formation of the radical $C_6H_5CHBr\dot{C}HCOOH$, no compounds carrying a bromine atom on the carbon adjacent to the phenyl group, excepting α,β-dibromohydrocinnamic acid, having been obtained as reaction products. The isolation of α,β-dibromohydrocinnamic acid, which might be supposed to have been produced from the above radical and bromine, cannot be adduced as evidence in support of the formation of the radical in question, because, in view of the reactivity of such intermediate radicals in general, there is no reason why this radical should not react with oxygen as well, if not with hydrogen bromide, giving rise to products carrying a bromine atom on the carbon adjacent to the phenyl group.

The formation of the radical $C_6H_5\dot{C}HCHBrCOOH$ in preference to the alternative radical $C_6H_5CHBr\dot{C}HCOOH$ is easily accounted for on the basis of considerations analogous to those advanced by Mayo and Walling by the reasonable assumption that the former will be more stable than the latter because of the greater resonance energy due to the conjugation of the free valency electron on the β-carbon atom with the phenyl group than that due to the conjugation of the free valency electron on the α-carbon atom with the carboxyl group.

It was argued previously[5] that if cinnamic acid was to add hydrogen bromide to give only β-bromohydrocinnamic acid even under the conditions favourable to the abnormal addition, this might well be attributable to the circumstances that the theoretically more stable radical $C_6H_5\dot{C}H$-$CHBrCOOH$, owing to its relatively great stability, reacts with hydrogen bromide with more difficulty than does the isomeric β-bromo radical. However, the possibility of the formation of β-bromohydrocinnamic acid through the chain mechanism under usual oxygenic conditions can now be ruled out, for, in the first place, the reaction under such conditions did not appear to be faster than that in the presence of catechol, and secondly, in the reaction with a large amount of oxygen it was demonstrated that only the α-carbon atom of cinnamic acid is attacked by bromine atoms.

β-Bromohydrocinnamic acid is formed only by the normal addition of hydrogen bromide, and that even in the presence of benzoyl peroxide. As the normal reaction is a slow one, it could not compete to advantage

with the abnormal addition which should produce α-bromohydrocinnamic acid through the chain mechanism, if the radical $C_6H_5\dot{C}HCHBrCOOH$ were active enough to react readily with hydrogen bromide to initiate the chain.

In view of the relative stability of the radical postulated above it is supposed that the dimerization of it may have taken place. Although no compound resulting from the dimerization was found, this will not detract from the possibility of the operation of the reaction mechanism involving the free radical, inasmuch as the dimerization of usually scarce radicals would take place only under exceptionally favourable conditions provided by a very inert medium containing no reactive substances, such as oxygen.

Experimental Part

Materials. Hydrogen bromide was generated by dropping bromine on hot tetralin, and passed through a bottle containing cold tetralin, and then through a tube containing glass wool sprinkled with phosphorus pentoxide. For experiments in sealed tubes the hydrogen bromide was collected in a tube cooled with liquid air. Then the condensed hydrogen bromide was subjected to repeated fusion and solidification in vacuum to eliminate traces of incondensable gases. Cinnamic acid was synthesized from benzaldehyde, acetic anhydride, and anhydrous sodium acetate, and recrystallized from alcohol several times. It melted at 132.0–2.5°C. Carbon tetrachloride was refluxed with an alkaline permanganate solution, dried with anhydrous calcium chloride, and distilled. Benzene was shaken with concentrated sulphuric acid several times until the sulphuric acid layer was colourless, dried with calcium chloride, and distilled over sodium.

The Addition of Hydrogen Bromide to Cinnamic Acid in Benzene in a Sealed Tube. In a glass tube with a capacity of 70 c.c. cinnamic acid (4 g.) and benzene (15 c.c.) together with benzoyl peroxide (0.2 g.) or catechol (0.1 g.) were placed, and the tube was connected to the vacuum line. In order to remove oxygen the contents of the tube were solidified by cooling with liquid air, and the tube was evacuated with a mercury diffusion pump. The contents were then melted, again solidified, and the tube was evacuated to 0.0005 mm. of mercury. The procedure was repeated three times. Then a measured quantity of hydrogen bromide (1.5 c.c. at the temperature of solid carbon dioxide and ether) was condensed on the top of the solidified mixture, and the tube was sealed off. The tube was kept at about 60° in a hot water bath in the day-time. After five days the reaction tube was opened, and the benzene solution was filtered from a precipitate. The solid product (m.p. 134°, 4.9 g. in the experiment with catechol) which was already nearly pure was recrystallized from carbon disulphide and identified as β-bromohydrocinnamic acid. In the experiment with benzoyl peroxide, in addition to the above product (4.1 g.), on evaporation of the filtered benzene solution a solid residue (1.2 g., m.p. 98–123°) was obtained, from which a further crop of β-bromo-

hydrocinnamic acid was separated.

The Action of the Mixture of Hydrogen Bromide and Oxygen on Cinnamic Acid in the Dark. The essential part of the experiments has already been described above. After the reaction was complete, the deposit (α, β-dibromohydrocinnamic acid, m.p. 192°) was separated from the solution, weighed (10.4 to 11.4 g.) and analyzed for bromine (found: Br, 48.2%). On recrystallization from carbon disulphide the bromine content was improved to 51.2% (calculated for $C_9H_8O_2Br_2$: Br, 51.9%). By removing the solvent from the solution under diminished pressure a residue (2.8 to 3 g.) consisting of a yellow oil and a small amount of a crystalline substance identified as α,β-dibromohydrocinnamic acid were obtained. The oil was dissolved in ether, dried with anhydrous sodium sulphate, and distilled under reduced pressure. The lachrymatory distillate, which passed over at 78–82° under 0.75 mm., was analyzed for bromine (found: Br, 39.2%). By cooling this distillate in an ice-box plate crystals were obtained, which after recrystallization from alcohol melted at 50–51° (found: Br, 40.2%; calculated for C_8H_7OBr: Br, 40.2%). The melting point of the substance was not depressed on admixture with an authentic specimen of ω-bromoacetophenone.

The gas issuing from the reaction vessel was passed through a bottle containing water and then through one containing an aqueous barium hydroxide solution. The precipitated barium carbonate was dried and weighed. The amount of carbon dioxide evolved was estimated at 0.089 to 0.209 mole per mole of the cinnamic acid used.

The product of addition of hydrogen bromide to cinnamic acid is β-bromohydrocinnamic acid either under the antioxidant condition or in the presence of benzoyl peroxide.

Summary

The action of the mixture of hydrogen bromide and oxygen on cinnamic acid in carbon tetrachloride produces ω-bromoacetophenone together with α,β-dibromohydrocinnamic acid. It is concluded that the free radical $C_6H_5\dot{C}HCHBrCOOH$ is formed in the intermediate stage in accord with the expectation from theoretical considerations concerning the stability of radicals. The radical, owing to its stability, does not react with hydrogen bromide to give α-bromohydrocinnamic acid, but reacts, on one hand, with oxygen ultimately to give ω-bromoacetophenone after disrupture of carbon dioxide and, on the other hand, with bromine or hydrogen bromide, as detailed in the text, to give α, β-dibromohydrocinnamic acid.

The authors express their sincere thanks to Prof. Y. Urushibara for his kind guidance and encouragement throughout this work.

Chemical Institute, Faculty of Science,
University of Tokyo.

New Diffusion Pump Oil—Higher Monoalkyl-naphthalenes.

By Tutomu KUWATA, Sin-ichi TOMIYAMA and Masayasu TAKAO.

(Received November 16, 1948.)

Introduction. C. R. Burch[1] who first used organic liquid, in place of mercury, for diffusion pump medium obtained the vacuum of 10^{-6} mm-Hg, using a special fraction of lubricating oil of paraffin series and no cooling trap. Hickman and his collaborators[2] reported later that esters of phthalic acid or sebacic acid have suitable properties as diffusion pump oil and obtained the high vacuum of 1×10^{-7} mm-Hg by using octyl phthalate (Octol) and octyl sebacate (Octoils). Sagane, Haruta and others[3] have tested a synthetic oil, "Kao" oil, which was prepared from olefine hydrocarbons derived from higher fatty acids using aluminium chloride as a polymerization catalyst and showed the oil to be as good as Apiezon B or Octoil S in regard to vacuum and stability when used as diffusion pump oil.

One of the present authors (T. Kuwata) has found a new synthetic method of preparing higher alkyl-naphthalenes from higher alcohols and naphtahlene by the dehydrating and alkylating action of Japanese acid clay.[4] The process is relatively simple and gives good yield of condensate. For example, when 250 g. of cetanol and 100 g. of naphthalene were heated in the presence of 75 g. of activated Japanese acid clay, eliminatoin of water began at the neighbourhood of 190°C. The heating was continued at 190–210°C. until the evolution of water vapour ceased, the catalyst was filtered off, and then the resultant oil was distilled under reduced pressure, obtaining 260 g. of the produc of which ca. 45% were monoalkyl-naphthalene and 35% were dialkyl-naphthalene with small amount of tri-derivative. The saturated paraffin hydrocarbon containing no naphthalene ring amounted to ca. 10% of the product.

The present report concerns the properties of some of higher alkyl-naphthalenes, such as monododecyl, monotetradecyl, monohexadecyl and monooctadecyl-naphthalenes obtained by the process above mentioned.

Preparation and Properties of Monoalkyl-naphthalenes. 20 kg. of crude higher alcohols (Sp. v. 9.6, Ac. v. 212.5), which were prepared by the catalytic reduction of cocoanut oil, were rectified under reduced pressure using a column 1 m. long filled with Stedman's wire gauze corn, and pure dedecyl alcohol was obtained. The higher fraction was changed into acetic ester, and repeating its fractional distillation, pure acetic ester of tetradecyl alcohol was obtained. Pure hexadecyl and octadecyl

(1) C. R. Burch, *Proc. Roy. Soc.*, **A, 23** (1929), 271.
(2) Hickman, *Frank. Inst.*, **321** (1946), 381.
(3) Sagane etc., *Kagaku*, **14** (1944), 315.
(4) T. Kuwata *J. Chem. Soc., Japan, Ind. Section*, **52** (1949), 146.

alcohols were prepared by the repeated fractionation of 3 kg. of crude cetanol (Sp. v. 0.5, Ac. v. 186).

The higher alcohols thus obtained had the following properties.

Table 1. Properties of Pure Higher Alcohols and their Acetic Esters.

		Dodecyl alcohol	Tetradecyl alcohol	Hexadecyl alcohol	Octadecyl alcohol
Acetate	Boiling point (°C/mm.)	—	129-131/1	147-150/1	166-168/1
	Sp. v. obs.	—	220.1	199.5	178.8
	calc.	—	219.0	199.0	179.6
	M. p. obs.	—	—	21.5-22.0	30.0-30.5
	lit.	—	—	22.7	31
Free alcohol	B. p. (°C/mm.)	110-112/1	125-126/1	142-144/1	159-161/1
	Ac. v. obs.	241.9	219.8	199.2	179.1
	cal.	243.8	219.0	199.0	179.6
	M. p. obs.	24.5-25.0	37.0-35.5	48.5-49.5	58-59
	lit.	24	38	50	59

The dehydrating condensation of these alcohols with naphthalene was carried out at 200°C. for 60 minutes. The resulant product was purified by the fractional distillation under the pressure of 1×10^{-2} mm-Hg and then 5×10^{-3} mm-Hg. The properties of monoalkly-naphthalenes thus obtained were shown in Table 2.

Table 2. Properties of Higher Monoalkyl-naphthalenes.

		Dodecyl-naphthalene	Tetradecyl-naphthalene	Hexadecyl-napnthalene	Octadecyl-naphthalene
Boiling pt. (1 mm-Hg)		180-182°C.	198-200°C.	212-214°C.	226-228°C.
Specific gravity (30°/4°)		0.9107	0.9055	0.8991	0.8942
Refractive index (30°/D)		1.5262	1.5240	1.5219	1.5192
Specific refraction (r_D^{30})		0.3371	6.3379	0.3392	0.3395
Mol. refraction	obs.	99.61	108.80	118.48	127.73
	calc.	99.06	106.30	115.43	123.67
Mol. weight	obs.*	295	322	349	376
	calc.	296	324	352	379
Solidifying pt.		-42°C.	—	—	-16°C.
Viscosity	210°F	37.0	39.4	41.7	44.6
(S. U. S.)	100°F	90.0	113.5	140.5	173.9
Viscosity index		6.16	59.5	74.1	97.6
Elementary analysis	C % obs.	88.82	89.42	88.36	88.13
	C % calc.	89.11	88.82	88.56	88.35
	H % obs.	10.87	11.46	11.47	11.70
	H % calc.	10.88	11.18	11.44	11.67

* Cryoscopic method.

The values cited in Table 2. differ from those reported by Mikeska and his collaborators,[5] i. e. n-octadecyl-naphthalene of Mikeska melted at 51–52°C. and had viscosity index of 144. The constitution of monoalkyl-naphthalenes of the present authors has not yet been confirmed, but they may be assumed to be 2-naphthyl alkanes.

Vacuum Test of Monoalkyl-Naphthalenes. The vacuum test of the oil was carried out by the diffusion oil pump of Hickman type. The pump was charged with the testing oil and put on action for 5–6 hours, and then heating was controlled at the intervals of 30 minutes so as to obtain the optimum vacuum which was measured by ionization gauge. The data are shown in Table 3.

In order to test the oxidation stability of the oils, the air was introduced into the acting pump, continuing the heating until the pressure dropped to atmospheric pressure. After the lapse of 2 minutes, the pump was put again on action, and the restoration time and maximum attainability of vacuum were observed. On repeating the same process for 4 times, the "Kao" oil showed the evident deterioration, while alkyl-naphthalenes rather shortened the restoration time and increased the maximum vacuum.

Table 3. The Highest Attainability of Vacuum.

Monododecyl-naphthalene	2.1×10^{-6} mm-Hg
Monotetradecyl-naphthalene	5.2×10^{-6} ,,
Monohexadecyl-naphthalene	4.5×10^{-6} ,,
Monooctadecyl-naphthalene	1.2×10^{-5} ,,
"Kao" oil	3.0×10^{-6} ,,

Among the alkyl-naphthalenes used in the present studies, monododecyl-naphthalene was the most excellent as diffusion pump oil in regard to the action of the pump at relatively low temperature and the attainability of high vacuum.

Summary. Some monoalkyl-naphthalenes were prepared by the condensation of naphthalene and respective alcohols using activated Japanese acid clay as a condensing catalyst. The constitution of the alkyl-naphthalenes was assumed to be 2-naphthyl alkanes. The alkyl-naphthalenes were shown to be usable as good diffusion pump oil. The oils were very resisting for oxidation.

The authors wish to express their best thanks to Dr. Imachi of Horikawa Factory of Tokyo-Shibaura Electric Co. for his kind and earnest aid in the vacuum tests.

Department of Applied Chemistry, Faculty of Engineering, University of Tokyo.

(5) Mikeska etc., *Ind. Eng. Chem.*, **29** (1937), 970.

The Scission Reactions of the Oxido Ring in Cholesterol Oxides.[1]

By Yoshiyuki URUSHIBARA and Misao CHUMAN.

(Received January 18, 1949.)

The scission reactions of the oxido ring in α- and β-cholesterol oxides have been studied in this laboratory since one of the authors[2] derived the configurations of these stereoisomeric oxido compounds and related diols from that of the so-called α-cholestanetriol which had been determined to be cholestanetriol-(3β,5α,6β) (III) by Ellis and Petrow.[3] A β-oxido structure (II) of β-cholesterol oxide was concluded from the change of the α-cholestanetriol (III) to this oxide through a 5-chlorodiol-(3β,6β) (IV), and consequently an α-oxido configuration (I) was assigned to α-cholesterol oxide. Further, the Δ^4-cholestenediol-(3,6) melting at 257–258° was found to be Δ^4-cholestenediol-(3β,6β) (V), because it is obtainable from the triol (III) by a Darzens dehydration of its diacetate followed by saponification, and the 6-isomeride melting at 178–179° proved to be Δ^4-cholestenediol-(3β,6α) (VI). The cholestanediol-(3,6) melting at 194–195° was given a configuration of cholestanediol-(3β,6β) (VII), because it is obtained by a catalytic reduction of the higher melting unsaturated diol (V), and hence its 6-isomeride melting at 216° should be cholestanediol-(3β,6α) (VIII).

Reduction of Cholesterol Oxides with Sodium and Amyl Alcohol.[4]

As described in details elsewhere,[4] on reduction with sodium and amyl alcohol α-cholesterol oxide (I) gave cholestanediol-(3β,6α) (VIII), while pure β-cholesterol oxide (II), prepared from α-cholestanetriol (III) through the chlorohydrin (IV), was reduced to the same cholestanediol-(3β,6α) (VIII). The formation of cholestanediol-(3β,6α) from the α-oxide appeared quite natural, but an explanation was required for the formation of a cholestane derivative with a 6α-hydroxyl group from the β-oxide (II). An inversion of the β-oxide to the α-isomeride prior to reduction under the conditions of the reaction, especially by the action of sodium amylate, was first suspected but disproved by experiments: When the β-oxide was heated with sodium amylate it was reduced to cholestanediol-(3β,6α) while the α-oxide was not reduced when treated similarly, and the β-oxide was not changed when heated with sodium ethylate. Therefore, it is very probable that the reduction of the β-oxide to cholestanediol-(3β,6α) did not go through the α-oxide.

(1) Abstracts from the doctor theses by M. Chuman. For originals consult the footnotes under respective subtitles.

(2) Y. Urushibara, this Bulletin, **16** (1941), 182.

(3) B. Ellis and V. A. Petrow, *J. Chem. Soc.*, **1939**, 1078.

(4) M. Chuman, *J. Chem. Soc. Japan*, **64** (1943), 1369.

When the 3,6-diol was formed from the β-oxide by reduction, the oxido ring was opened between carbon atom 5 and the oxido oxygen atom. Then the formation of a cholestane derivative from the β-oxide can be understood on the assumption of a Walden inversion at carbon atom 5; but a 6β-hydroxyl group should be produced from the oxygen atom in β-configuration. Consequently, it must be assumed that the 6α-hydroxyl group in the product was formed through an inversion from the primarily introduced 6β-hydroxyl group. Experiments showed it was really the case: When cholestanediol-(3β,6β) (VII), prepared from 6-keto-cholestanol by catalytic reduction,[5] was heated with sodium amylate, it was transformed into cholestanediol-(3β,6α) (VIII). Such an inversion of a newly formed hydroxyl group would have been possible also in the reduction of α-cholesterol oxide, if the hydroxyl group had had an unstable configuration; but the 6α-hydroxyl group formed primarily by the scission of the α-oxido ring was stable to sodium amylate and remained without inversion. The 3β-hydroxyl group in the reduction product is considered stable to alcoholates as so is that in cholestanol. A problem may arise rather from the fact that the oxido ring in α-cholesterol oxide is opened between carbon atom 5 and the oxygen atom by the action of sodium and amyl alcohol, because it is the only exceptional behaviour of the α-oxide ever experienced in its scission reactions.

Catalytic Reduction of Cholesterol Oxides.[6]

Earlier experiments on catalytic reduction showed that α-cholesterol oxide is difficultly reduced while β-cholesterol oxide is reduced too far to cholestane and cholestanol. Even such undesired over-reduction indicated that the β-oxide is not reduced to a coprostane derivative which might be expected from the configuration given to it. Catalytic reduction of the acetates with platinum oxide in glacial acetic acid was finally successful both in reducing the α-oxide and in obtaining from the β-oxide a product retaining the oxygen atom of the oxido ring. Thus, β-cholesterol oxide acetate (II') gave cholestanediol-(3β,6β) 3-acetate (VII'), m.p. 155–156°, along with cholestane and cholestanol acetate. Hydrolysis gave free cholestanediol-(3β,6β) (VII) idential with the specimen prepared from 6-keto-cholestanol by catalytic reduction.

A similar reduction of α-cholesterol oxide acetate (I') yielded a product melting at 178–179° and sparingly soluble in alcohol. It remained unchanged on boiling with acetic anhydride, thus showing the newly formed hydroxyl group, if any, was tertiary. Saponification with alcoholic potash gave a substance melting at 220–221° and difficultly soluble in ether. Analysis gave numbers calculated for a cholestanediol. The diol was oxidized with chromic acid to a substance melting at 231–232°, and dehydration of the latter produced the known Δ^4-cholestenone (XI). Hence, the new diol is a 3,5-diol, and the oxido ring was opened by reduc-

(5) R. E. Marker and J. Krueger, *J. Am. Chem. Soc.*, **62** (1940), 79.
(6) M. Chuman, *J. Chem. Soc. Japan*, **64** (1943), 1486.

tion between carbon atom 6 and the oxygen atom; and thus the 5-hydroxyl group must necessarily possess an α-configuration. Consequently, the diol is cholestanediol-(3β,5α) (IX), and the substance, m.p. 178–179°, obtained primarily by the reduction of α-cholesterol oxide acetate is its 3-monoacetate (IX'). The product, m.p. 231–232°, from the oxidation of the free diol which gave Δ^4-cholestenone by dehydration is 5α-hydroxy-cholestanone-(3) (X). Designation "α" after position number "5" may be omitted in the names of the cholestane derivatives, because it is implicitly expressed by term "cholestane".

The course of reactions starting from a 5,6α-oxido steroid and leading to an α,β-unsaturated 3-keto-steroid was successfully applied to the synthesis of testosterone[7] and progesterone.[8]

Recently the authors became aware of the publication of similar works on catalytic reduction of cholesterol oxides by Stavely[9] and by Plattner and others,[10] although the original papers are not available here. The former, reducing α-cholesterol oxide with a palladium catalyst and obtaining cholestanediol-(3,5) monoacetate after acetylation, seems to have suggested that when an ethylene oxide ring is opened by hydrogenation the hydroxyl group formed will be attached to the carbon atom carrying the smaller number of hydrogen atoms. The latter reduced both α- and β-cholesterol oxide acetates with the same catalyst as used by the present authors and obtained similar results. The melting points of their products as quoted in the *Chemical Abstracts*, however, do not show any good coincidence with those obtained for the corresponding substances by the present authors, some being higher and others lower. The discrepancies in the melting points may be due to either different purities or otherwise possible polymorphism of crystals.

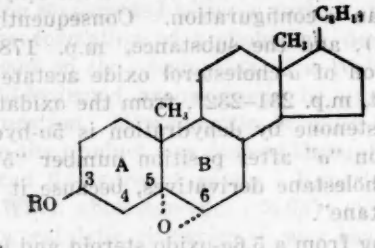
Action of Aluminium Amalgam and of Aluminium Isopropylate and Isopropyl Alcohol on Cholesterol Oxides.[11]

Attempted reduction with aluminium amalgam and with aluminium isopropylate and isopropyl alcohol yielded none of reduced compounds. α-Cholesterol oxide was attacked by neither of the reagents. β-Cholesterol oxide, on the other hand, was hydrated to cholestanetriol-(3β,5α,6β) (III) on treatment with the former reagent in hydrous alcohol, while it was isomerized to Δ^4-cholestenediol-(3β,6β) (V) by the latter reagent.

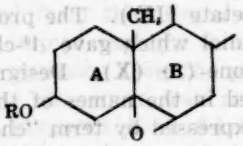
Hydration of Cholesterol Oxides.[12]

α-Cholesterol oxide is long known to give α-cholestanetriol, namely, cholestanetriol-(3β,5α,6β) (III), when heated with water in a sealed tube, while the hydration reaction of β-cholesterol oxide had not yet been studied

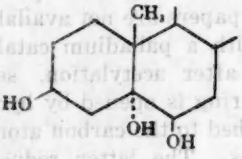
(7) Y. Urushibara and M. Chuman, this Bulletin, **22** (1949), 1.
(8) Y. Urushibara, M. Chuman, and S. Wada, this Bulletin, in press.
(9) H. E. Stavely, *Chemical Abstracts*, **37** (1943), 652.
(10) Pl. Plattner, Th. Petrzilka, and W. Lang, *Chemical Abstracts*, **38** (1944), 6295.
(11) M. Chuman, *J. Chem. Soc. Japan*, in press.
(12) M. Chuman, *J. Chem. Soc. Japan*, in press.



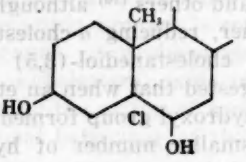
(I) R = H: α-Cholesterol oxide
(I′) R = CH_3CO: Acetate of I



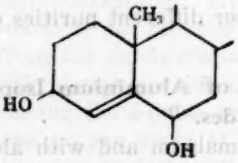
(II) R = H: β-Cholesterol oxide
(II′) R = CH_3CO: Acetate of II



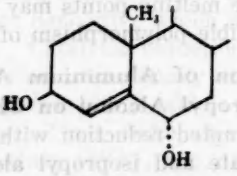
(III) α-Cholestanetriol,
Cholestanetriol-(3β, 5α, 6β)



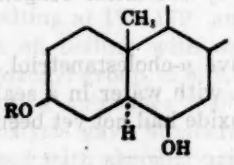
(IV) 5-Chloro-cholestanediol-(3β, 6β)



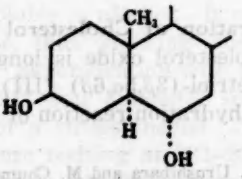
(V) Δ^4-Cholestenediol-(3β, 6β)



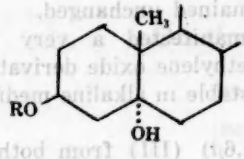
(VI) Δ^4-Cholestenediol-(3β, 6α)



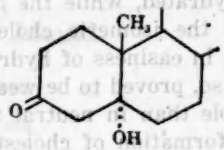
(VII) R = H: Cholestanediol-(3β, 6β)
(VII′) R = CH_3CO: 3-Acetate of VII



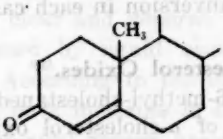
(VIII) Cholestanediol-(3β, 6α)



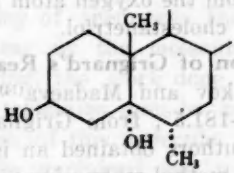
(IX) R = H: Cholestanediol-(3β, 5α)
(IX′) R = CH_3CO: 3-Acetate of IX



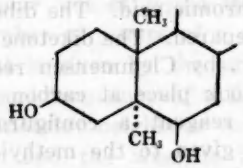
(X) 5α-Hydroxy-cholestanone-(3)



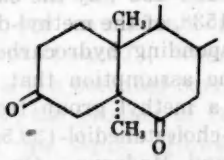
(XI) Δ^4-Cholestenone



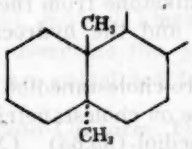
(XII) 6α-Methyl-cholestanediol-(3β, 5α)



(XIII) 5α-Methyl-cholestanediol-(3β, 6β)



(XIV) 5α-Methyl-cholestanedione-(3, 6)



(XV) 5α-Methyl-cholestane

with a pure specimen. The hydration reactions of these isomeric oxides were compared under various conditions with the following results:

The β-oxide did not react with water at such temperatures (120°, 14 hours, and 160°, 10 hours) as were high enough to cause the hydration of the α-oxide, but gave the same α-cholestanetriol (III) at a much higher temperature (over 200°, 10 hours). With slightly acidic water (one drop of 10% sulfuric acid to 1 c.c.) both oxides were easily hydrated to the triol (at 120°, 10 hours). With slightly alkaline water (one drop of 5% caustic potash to 1 c.c.), however, neither reacted (at 120°, 10 hours). With a stronger aqueous alkali (2% potassium hydroxide solution) and at a higher temperature (160–170°, 10 hours) the α-oxide was partly

(20%) hydrated, while the β-oxide still remained unchanged.

Thus the isomeric cholesterol oxides manifested a very striking difference in easiness of hydration, and, as ethylene oxide derivatives are generally so, proved to be weak to acid and stable in alkaline media, much more stable than in neutral water.

The formation of cholestanetriol-(3β,5α,6β) (III) from both α- and β-cholesterol oxides indicates that the oxido ring is opened by hydration between carbon atom 6 and the oxygen atom in the α-oxide and between carbon atom 5 and the oxygen atom in the β-oxide, and the carbon atom cut off from the oxygen atom undergoes an inversion in each case to give the same cholestanetriol.

Action of Grignard's Reagent on Cholesterol Oxides.[13]

Ushakov and Madaeva[14] obtained a 6-methyl-cholestanediol-(3,5), m.p. 181–181.5°, from Grignard's reaction of α-cholesterol oxide. The present authors obtained an isomeric methyl-diol, m.p. 195–196°, by the action of methyl-magnesium iodide on β-cholesterol oxide, and demonstrated that the new methyl-diol was a 5-methyl-diol-(3,6) by obtaining a diacetate, m.p. 132–133°, by the action of acetic anhydride and a diketone, m.p. 194–195°, by the oxidation with chromic acid. The dibenzoate, m.p. 152–153°, of the methyl-diol was also prepared. The diketone yielded the corresponding hydrocarbon, m.p. 94–95°, by Clemmensen reduction.

On the assumption that no inversion took place at carbon atom 6 obtaining a methyl group from Grignard's reagent a configuration of 6α-methyl-cholestanediol-(3β,5α) (XII) was given to the methyl-diol of Ushakov and Madaeva. On the other hand, a structure of 5α-methyl-cholestanediol-(3β,6β) (XIII) was deduced for the 5-methyl-diol-(3,6), because β-cholesterol oxide gives cholestane derivatives in all other scission reactions. Consequently, the diketone from the 5-methyl-diol is 5α-methyl-cholestanedione-(3,6) (XIV) and the hydrocarbon from the diketone 5α-methyl-cholestane (XV).

The chlorohydrin, 5-chloro-cholestanediol-(3β,6β) (IV), obtained by the action of hydrogen chloride on cholestanetriol-(3β,5α,6β) (III), yielded the same 5-methyl-cholestanediol-(3β,6β) (XIII) on treatment with methyl-magnesium iodide.

In a separate paper a stereochemical interpretation of the scission reactions of cholesterol oxides will be presented, and in another it will be shown that the α- and β-oxides of Δ^5-cholestenone correspond respectively to β- and α-cholesterol oxides in the behaviours in scission reactions.

Chemical Institute, Faculty of Science,
University of Tokyo.

(13) M. Chuman, *J. Chem. Soc. Japan*, in press.
(14) *Brit. Chem. Abst.*, **1939**, A (II), 367.

On the Viscosity of Liquid.

By Kunihiko KIGOSHI.

(Received October 1, 1948.)

Introduction. Up to this time, a number of theories on the viscosity of simple liquid were proposed by several authors,[1] each from a different point of view. Among these, H. Eyring's theory seems to be the most clear and general. But not in any of them was the shearing force caused by liquid viscosity made clear by the molecular kinetic theory. According to the idea of H. Eyring, the work done by shearing force on a molecule in the process of transition may be transferred to the potential energy barrier of transition of this molecule. However this approximation leaves something to be explained and it must be justified theoretically or experimentally.

The present author intends to give a theory of viscosity based on the similar idea of liquid structure used by Eyring and others. Thus the number of jumps of a molecule from one equilibrium position to the next is given by the simple formula $\nu \exp(-\omega/kT)$, where ν is the vibrational frequency of a liquid molecule, ω is a potential barrier formed by the nearest neighbour molecules, and kT, the product of Boltzmann's constant and the absolute temperature of the liquid. However, in a non-uniform flow a difference in a number of jumps between different directions may be caused not by a difference of ω, as has been usually considered, but by the directional difference of T. In this case T is not a temperature but a mean mutual kinetic energy of two molecules which effectively exerts to overcome the potential barrier. A gradient of flow and shearing force are calculated from this standpoint.

Shearing Force in a Non-Uniform Flow. Molecular arrangement in a liquid may be considered as follows. Around one molecule, Z_g nearest neighbour sites are located on a spherical shell with a radius R. Among these sites Z_m are occupied by the nearest neighbour molecules. We may neglect molecular interaction except the force f between the nearest neighbours. This force is determined by the distance between two molecules, which varies from R by the thermal motion of molecules. There exists such a force between each molecular pair, and f is the mean value of these forces. Therefore we can consider f as a function of R and θ, where θ is a variable expressing the mutual thermal motion of two molecules and we may give it the same dimension as tem-

(1) H. Eyring, *J. Chem. Phys.*, 4 (1936), 238; S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", 480 (1941); J. Frenkel, *Trans. Faraday Soc.*, 33 (1936), 58; S. Kaneko, This Bulletin, 15 (1940), 276.

CHEMISTRY RAIT LIBRARY

(20%) hydrated, while the β-oxide still remained unchanged.

Thus the isomeric cholesterol oxides manifested a very striking difference in easiness of hydration, and, as ethylene oxide derivatives are generally so, proved to be weak to acid and stable in alkaline media, much more stable than in neutral water.

The formation of cholestanetriol-(3β,5α,6β) (III) from both α- and β-cholesterol oxides indicates that the oxido ring is opened by hydration between carbon atom 6 and the oxygen atom in the α-oxide and between carbon atom 5 and the oxygen atom in the β-oxide, and the carbon atom cut off from the oxygen atom undergoes an inversion in each case to give the same cholestanetriol.

Action of Grignard's Reagent on Cholesterol Oxides.[13]

Ushakov and Madaeva[14] obtained a 6-methyl-cholestanediol-(3,5), m.p. 181–181.5°, from Grignard's reaction of α-cholesterol oxide. The present authors obtained an isomeric methyl-diol, m.p. 195–196°, by the action of methyl-magnesium iodide on β-cholesterol oxide, and demonstrated that the new methyl-diol was a 5-methyl-diol-(3,6) by obtaining a diacetate, m.p. 132–133°, by the action of acetic anhydride and a diketone, m.p. 194–195°, by the oxidation with chromic acid. The dibenzoate, m.p. 152–153°, of the methyl-diol was also prepared. The diketone yielded the corresponding hydrocarbon, m.p. 94–95°, by Clemmensen reduction.

On the assumption that no inversion took place at carbon atom 6 obtaining a methyl group from Grignard's reagent a configuration of 6α-methyl-cholestanediol-(3β,5α) (XII) was given to the methyl-diol of Ushakov and Madaeva. On the other hand, a structure of 5α-methyl-cholestanediol-(3β,6β) (XIII) was deduced for the 5-methyl-diol-(3,6), because β-cholesterol oxide gives cholestane derivatives in all other scission reactions. Consequently, the diketone from the 5-methyl-diol is 5α-methyl-cholestanedione-(3,6) (XIV) and the hydrocarbon from the diketone 5α-methyl-cholestane (XV).

The chlorohydrin, 5-chloro-cholestanediol-(3β,6β) (IV), obtained by the action of hydrogen chloride on cholestanetriol-(3β,5α,6β) (III), yielded the same 5-methyl-cholestanediol-(3β,6β) (XIII) on treatment with methyl-magnesium iodide.

In a separate paper a stereochemical interpretation of the scission reactions of cholesterol oxides will be presented, and in another it will be shown that the α- and β-oxides of Δ^5-cholestenone correspond respectively to β- and α-cholesterol oxides in the behaviours in scission reactions.

Chemical Institute, Faculty of Science,
University of Tokyo.

(13) M. Chuman, *J. Chem. Soc. Japan*, in press.
(14) *Brit. Chem. Abst.*, **1939**, A (II), 367.